IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman, et al.

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For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231

DECLARATION OF Alexander P. Moravsky

I, Alexander P. Moravsky, hereby declare:

1. I reside at 7887 E. Uhl Street, Apt. #1004, Tucson, Arizona, USA. 85710

2. I am currently employed as Senior Scientist at MER Corporation, Tucson, Arizona, and have been so employed since 1999. My employment history since 1995 is set forth in the attached Resume of Alexander P. Moravsky, incorporated herein and made a part hereof.

3. I am currently involved in fullerene and related materials synthesis and property studies and have been so involved since 1991 and have extensive experience in this field with many achievements and publications, as set forth in my attached Resume.

4. I have earned Ph.D, M.Sc. and B.Sc. degrees in the fields, of Chemistry, Physics and Molecular and Chemical Physics, all as set forth in my attached Resume.

5. I have 8 patents, 240 scientific publications and 4 reviews as set forth in my attached Resume.

6. My areas of scientific and technical expertise are extensive and are outlined in further detail in my attached Resume.

7. I have read the publication entitled "Spectroscopy of Matrix-Isolated Carbon Cluster Molecules between 200 and 850 nm Wavelength" published in Surface Science, v.156, pp.814-821 (1985) by W.Kratschmer, N.Sorg and D.Huffman, and I am fully conversant with the technology described in this paper, which relates to an area within my technical and scientific expertise and experience.

8. I have evaluated the methods and apparatus described in this paper to determine the possibility of fullerene molecules formation in the operation of this apparatus under conditions employed in the methods described in that paper.

9. The paper describes experiments on vaporizing graphite in an electric arc operating in 10^{-6} Torr vacuum maintained in the chamber by a turbomolecular pump. Carbon vapor produced in the interelectrode space is then flowing through the high-vacuum chamber to a cryo-cooled surface where it is co-deposited with argon molecules, thus forming a layer of

solid argon with embedded carbon products. The carbon products in solid argon matrix have been studied by UV-vis spectrophotometry. The spectral features observed are attributed by the authors to small carbon clusters C_4 –C_8 stabilized in cold argon matrix against further extensive coalescence. This attribution is well grounded; the perfect resolution of vibronic structure of spectral features unequivocally evidences for small clusters of this size, as large clusters or fullerenes are incapable of revealing such fine resolution. No indication to the presence of fullerenes in the products can be found in the spectra, even in trace amounts. It can be thus concluded that fullerenes are not formed in the system, neither during any carbon vapor transformations on its way to the cold support, nor during thermal annealing of small carbon clusters in argon matrix that was performed in the work under consideration.

10. This early work described in this 1985 paper preceded the discovery of the carbon arc process for fullerene production, announced in 1990 in the journal NATURE [W.Kratschmer, L.D.Lamb, K.Fostiropolous, D.R.Huffman, Nature, vol.347, 354 (1990)]. The decisive reason for the success reported in 1990 was implementation of inert gas atmosphere instead of vacuum environment. Indeed, in multiple articles following the discovery, different research teams upon the studies of helium pressure dependence of fullerene yield reported that fullerenes have not been found in the products of carbon arc process performed in vacuum.

11. Further studies of the mechanism of fullerene formation in the carbon arc revealed why fullerenes are not formed in vacuum. Carbon arc originally generates small carbon clusters, predominantly C_2 and C_3. Further evolution of carbon vapor involves conversion of

small clusters into large clusters C_n, comprising linear carbon chains, then carbon cycles and eventually stable fullerenes. In the competing route the carbon soot is formed from carbon clusters. This competition is strongly dependent upon the presence of inert buffer gas (helium), which ensures the cooling of "hot" intermediate carbon products formed through condensation of smaller carbon particles, which is necessary for fullerene molecule formation. Without this cooling the intermediate carbon products dissociate back into smaller carbon clusters hence formation of fullerene molecules becomes impossible.

12. This conclusion is confirmed quantitatively by the detailed kinetic mechanism of fullerene synthesis in the arc reactor, which has been shown capable of predicting the yield of fullerenes in the arc process under various conditions [A.V.Krestinin, A.P.Moravsky, Chem.Phys.Lett., 286, 479-484 (1998)]. The quantitative model shows that with helium pressure decrease down to zero, the characteristic time of carbon vapor cooling grows to very large values and accordingly, the yield of fullerenes drops down to zero.

13. Optimal conditions for high fullerene yields in the carbon arc produced soot have been multiply studied by dozens of research groups around the world. A quantitative model examining processes of, and conditions for, producing fullerenes was the subject of work in which I was involved at the Russian Academy of Sciences, referenced in [A.V.Krestinin, A.P.Moravsky, Chem.Phys.Lett., 286, 479-484 (1998)], a copy of which is attached as Exhibit A. In this respect it is noteworthy that the best found conditions for fullerene synthesis in the arc, that are employed in many industrial and academic production units, are

very close to conditions for fullerene production first disclosed in the aforementioned Nature article by W.Kratschmer, D.R.Huffman et al. (100 Torr helium, etc).

14. From the above, it is concluded that no fullerenes are formed in the carbon arc in vacuum, as is extensively proven experimentally and quite clearly conceived theoretically.

I further declare that all statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. I acknowledge that willful false statements and the like are punishable by fine or imprisonment or both (18 U.S.C. §1001) and may jeopardize the validity of the application or any patent issuing thereon.

07.16.2002
Date

A. Moravsky
Alexander P. Moravsky, Ph.D.

Signed in Tucson, Arizona

PRESENT INTERESTS AND OCCUPATION

Dr. Moravsky is involved in fullerene and related materials synthesis and property studies since 1991 and has notable achievements in this field, namely: a) development of an advanced kinetic mechanism of fullerene formation in the arc and its use to essentially scale up the process of fullerene production, b) high-yield synthesis of multi-walled carbon nanotubes (MWNTs) in the arc and refining the mechanism of this process, c) elaboration of an advanced catalytic system for single-wall carbon nanotubes production, d) discovery of an arc system for efficient synthesis of double-walled carbon nanotubes, e) selective synthesis of edge-abundant carbon nanofibers and scaling up the VGCF production process, f) development of new systems for RF plasma assisted vapor growth of oriented carbon nanofibres, g) synthesis of large arrays of aligned multi-walled carbon nanotubes, h) preparation of bulk quantities of 100% pure multi-walled carbon nanotubes, i) discovery and development of the arc synthesis of carbyne materials, j) discovery and studies of the mechanism of the thermobaric process of fullerene polymerization in solids and of electropolymerization in solutions, k) discovery and mechanism studies of fullerene catalytic properties in high-temperature hydrocarbon transformations, l) development of new catalytic systems for fullerenes hydrogenation, m) discovery of persistent electric currents in aggregated MWNTs. He participates in multiple research projects on fullerene-related science both as a principal investigator and as an executive researcher. His extensive experience in fullerene, MW and SW carbon nanotubes science and technology is reflected in 150 papers and 4 Patents.

List of publications in fullerene science and technology. 1993-2001.

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Exhibit A

CHEMICAL PHYSICS LETTERS

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Mechanism of fullerene synthesis in the arc reactor

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Abstract

A mathematical model for the arc reactor which takes into account (a) cooling and mixing of carbon vapour with a buffer gas, (b) non-isothermal kinetics of carbon clusters growth and (c) formation of soot particles and heterogeneous reactions at their surface has been developed. The model gives quantitative coincidence of experimental data with calculated values both for the fullerene yield and ratio C_{70}/C_{60} in the products of the arc synthesis run under widely varied conditions. Numerical analysis of the model has shown that experimental data obtained for the arc synthesis strictly constrain the choice of the mechanism of fullerene formation. © 1998 Elsevier Science B.V.

1. Introduction

The mechanism of the formation of fullerenes from carbon vapour remains an intriguing problem since the discovery of the process. What special kind of transformations leads to the appearance of carbon cages under commonly used synthetic conditions? Experiments on resistive evaporation of two carbon rods with different degrees of enrichment in ^{13}C have shown that carbon vapour consists of the smallest clusters before the process of fullerene formation starts [1]. Experimental gas ion chromatography studies of the structure of carbon clusters lead to the formulation of possible paths of fullerene formation through the coagulation of monocycles and successive transformations of polycyclic structures into closed carbon shells [2–4]. Quantum calculations have shown [4] that concomitant liberation of vibrational energy (10–20 eV) is more than enough to afford annealing of a carbon cage to its most stable state. The search for new rearrangements of carbon cages that would transform the cage into the most thermodynamically stable state through the low energy barrier route is under way [5]. All these studies eventually are aimed at promoting better understanding of the kinetic mechanism of carbon vapour condensation and the formation of fullerene molecules.

The correspondence of reported kinetic schemes to the real mechanism of fullerene formation could be verified through mathematical modelling of the experimental apparatus and concomitant comparison of numerical results with experimental data. With regard to the solution of this task, the hitherto known models of the carbon vapour condensation process [6–8] are essentially incomplete and need to be extended by accurate consideration of the contributions of all processes influencing the chemical kinetics of carbon vapour condensation under actual experimental conditions. These are the cooling of the carbon vapour, liberation of heat at its condensation,

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formation of soot particles and heterogeneous reactions at their surfaces.

We used an advanced fullerene arc generator and obtained a comprehensive array of experimental data under strictly controlled and widely varied conditions, which is suited for the development and testing of a theoretical model. Two features of experimental data are important for the chemistry of fullerene formation and therefore deserve special attention. First, the maximum fullerene yield attained constitutes a value of 20–25%, which seems at first sight to be unexpectedly high if one takes into account the ready condensation of carbon vapour on soot particles. Second, we have recently found that the value of the C_{70}/C_{60} ratio is independent of arcing conditions and numerically equal to 0.2 within a low error of 1.5% [9]. These experimental data allow to assume that the quantitative model of the electric arc reactor could become a useful tool in the check of theoretical hypotheses for the mechanism of fullerenes synthesis. In this Letter, such a model is presented which considers all processes and phenomena important for the formation of fullerenes, namely (i) the outflow of the carbon vapour from the electric arc interelectrode gap, its blending with helium gas and thus cooling, (ii) the non-isothermal kinetics of the reactions of carbon vapour condensation, and (iii) the formation of soot particles and heterogeneous reactions at their surface. By means of numerical analysis of the model, we have constructed a scheme of chemical reactions for the condensation of carbon vapour, which quantitatively describes the yield of fullerenes in the electric arc reactor and the ratio C_{70}/C_{60} in the products of the synthesis. The same kinetic scheme has appeared suitable for the quantitative description of the thermodecay of fullerenes under shock tube conditions as well.

2. Description of the gas dynamics and the source of carbon vapour

The stream of carbon vapour from the arc region forms a turbulent flow that can be idealised as a so-called fan flow — a flat flow of cylindrical symmetry. We constrain considerations only to experiments where the turbulent transfer in the stream exactly controls the dynamics of carbon vapour mixing and cooling. It means that diffusion transfer of helium into the arc region remains negligibly small compared to the mass flow of carbon vapour from the gap. This condition is fulfilled when the arc gap, h_0, is small enough, which is usually the case for small arc currents with the other parameters kept constant. Under such circumstances the gas leaving the frames of the arc region can be treated as a pure (not diluted by helium) carbon vapour. Thus it becomes possible to calculate the velocity of the stream U_0 and the gas temperature T_0 on the border of the arc:

$$U_0 = \frac{V_{soot} R T_0}{2\pi r_0 h_0 P},$$

where V_{soot} is the rate of fullerene soot formation, P is helium pressure in the reactor and r_0 is radius of the electric rods. The vapour temperature T_0 in this case also easily stems from the equation:

$$P_{eq}(T_0) = P,$$

where P_{eq} is equilibrium pressure of the carbon vapour. As a result the inter-electrode gap volume can be excluded from the mathematical consideration of both chemistry and gas dynamics. Under typical conditions the pressure of helium in the reactor constitutes 100–760 Torr and the temperature of the vapour T_0 lies in the range of 3600–3900 K. Fullerenes are not formed in this region which is too hot. Other authors estimate the temperature of the gas in a carbon arc to be about 4000 K [10].

We have composed the model of the arc reactor as a Cauchy problem for the system of ordinary differential equations, which describes evolution of an elementary gas volume moving along the symmetry plane:

$$\frac{dc_i}{dt} = k_C(c_{0,i} - c_i) + f_i/[M], \quad i = 1,2,\ldots N$$

$$\sum_{i=1}^{N} c_i C_{p,i} \frac{dT}{dt} = \sum_{i=1}^{N} c_i C_{p,i} k_T (T_{at} - T) + f_T/[M]$$

$$t = \int_{r_0}^{r} U_m^{-1}(r)\,dr,$$

where $U_m(r)$ is the gas velocity along the plane of symmetry; c_i, $c_{0,i}$ are relative concentrations of chemical species including soot particles inside and outside the turbulent jet, respectively (the size distri-

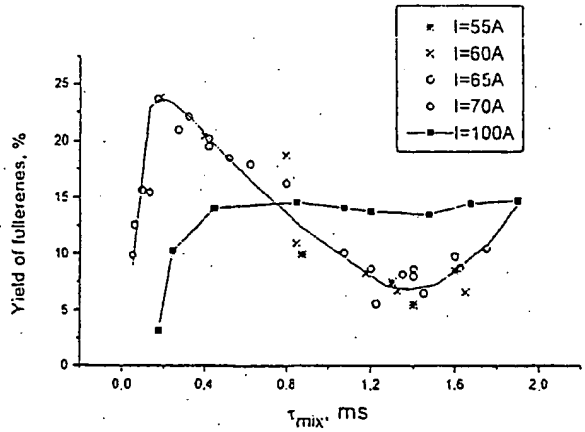


Fig. 1. Experimental data on the fullerenes yield represented as dependent on the characteristic time of turbulent cooling and mixing. All points corresponding to the arc currents of 55, 60, 65 and 70 Å are shown. The common solid line demonstrates the universal character of the dependence. The experimental points corresponding to the 100 Å series show that in this case the turbulent transfer does not control the process of mixing.

bution of soot particles was presented in the numerical code by sectional division as in Ref. [11]); T, T_{at} are the temperature values inside and outside the turbulent jet, respectively; $[M]$ is the total molar concentration of the gas; $C_{p,i}$ is the heat capacity of ith component at constant pressure; f_i, f_T are the chemical sources of the species and the heat; k_C, k_T are the rate constants of turbulent mass and heat transfer which are calculated according to the semiempirical theory of a free turbulent jet [12]:

$$k_C = \frac{0.32}{\tau_{mix} + 2t}, \quad k_T = \frac{0.64}{\tau_{mix} + 2t},$$

$$\tau_{mix} = \frac{r_0}{U_0}\left(\frac{r_0}{h_0}\right)^{0.5} = \frac{2\pi r_0^{2.5} h_0^{0.5}}{V_{soot} RT_0} P$$

The only parameter in the model which determines the rate of turbulent mixing and cooling τ_{mix}, as the expression above shows, depends on the arc process parameters.

In Fig. 1 the experimental data for the experiments carried out at low arc currents are represented as a function of that parameter. Really, the experimental points obtained under various arc currents, helium pressures and interelectrode gaps are grouped around a universal curve, pictorially presented as a solid line in Fig. 1. For the arc current of 100 Å, the fullerene yield is constant with respect to variation of the turbulent mixing rate parameter τ_{mix}. This infers that another process, i.e. diffusion transfer, controls mixing and cooling in this case which is characteristic of wide gaps.

3. Description of chemical reactions

To simplify the description of the chemical kinetics of the carbon vapour condensation process, we related the structure of a cluster to its size. All of the clusters containing less than 32 carbon atoms are considered to be chains, cycles and polycycles while clusters of more than 32 atoms are related to fullerene shells. The scheme of chemical reactions is shown in Fig. 2 and has the following features: (i) all of the possible coagulation reactions which yield chains, cycles and polycycles are taken into account; (ii) all of the coagulation reactions between small clusters which yield fullerene shells containing 32–46 C-

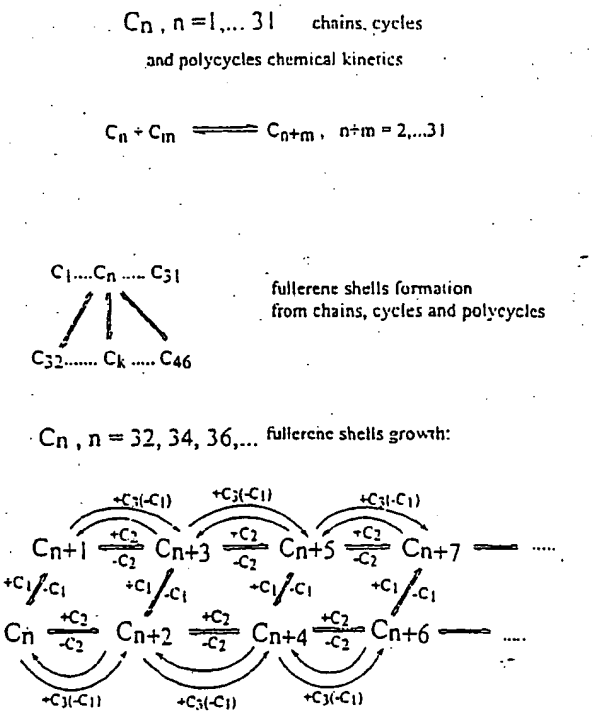
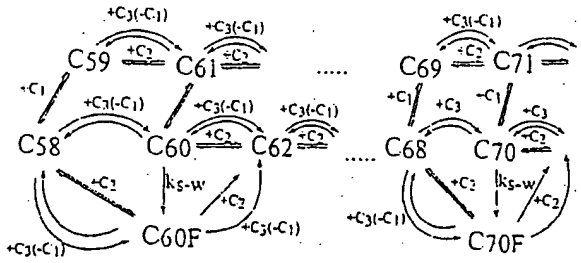
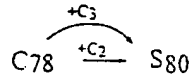


Fig. 2. Scheme of the chemical reactions for the condensation of carbon vapour.



Soot particles ($S_m = C_m$ with m >79) formation:



Heterogeneous reactions for all C_n, n=1-79:

$$S_m + C_n \longrightarrow S_{m+n}$$

Fig. 3. Reactions of the perfect fullerene molecules C_{60F} and C_{70F} formation, adopted in the scheme. Schematic of soot particles formation and heterogeneous reactions of the carbon clusters at the soot surface.

atoms are also taken into account; (iii) the closed-shell growth is considered to occur solely by means of implanting C_2 fragments into a shell in the reactions with the participation of C_2 or C_3 clusters; (iv) the soot particle formation and heterogeneous reactions of their growth via addition of carbon clusters of any size are considered in the scheme.

The C_{60} and C_{70} molecules (denoted as C_{60F} and C_{70F}) are formed in the scheme in two types of reactions (Fig. 3). The first one includes the monomolecular rearrangement similar to the Stone–Wales transition of the defect C_{60} or C_{70} clusters to the C_{60F} and C_{70F} molecules, respectively. The second one includes the channels of fullerene growth reactions that lead directly to perfect fullerene structures (C_{60F} and C_{70F}). The enthalpy and entropy values used for the carbon clusters sized below C_{10} and for individual C_{60F} and C_{70F} clusters have been reported [13–16]. The corresponding values for the rest of the carbon species are calculated from an appropriate piece-linear approximation (Fig. 4).

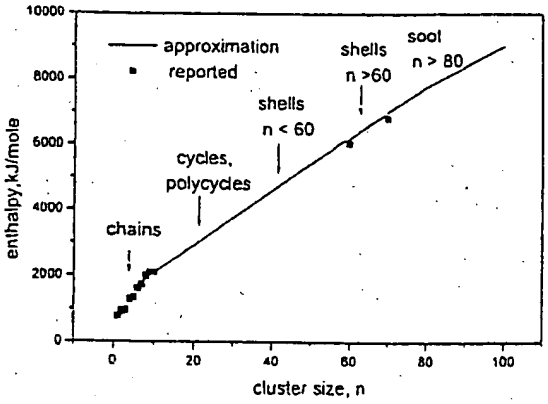


Fig. 4. Dependence of the enthalpy of formation of carbon clusters at 3000 K with their size.

4. Comparison with experimental data and discussion

The kinetic scheme developed is sufficient to fit quantitatively the experimental data on the thermodecay of C_{60} and C_{70} fullerenes in shock tubes well. The corresponding experimental results have been published [17]. Comparison of calculations with these experiments will be published elsewhere.

Fig. 5 represents experimental and calculated data for the arc reactor. Quantitative coincidence has been reached for the fullerene yield for pressures below 400 Torr where the turbulence controls the mixing process as is assumed in the model. The C_{70F}/C_{60F} ratio lightly drifts from 0.2 to 0.24, compared to the experimental value of 0.2. It should be stressed that it is not so simple a problem to satisfy limitations stated above. We examined many different kinetic schemes of fullerene formation before this scheme was developed. Here we summarise briefly the conclusions of this work.

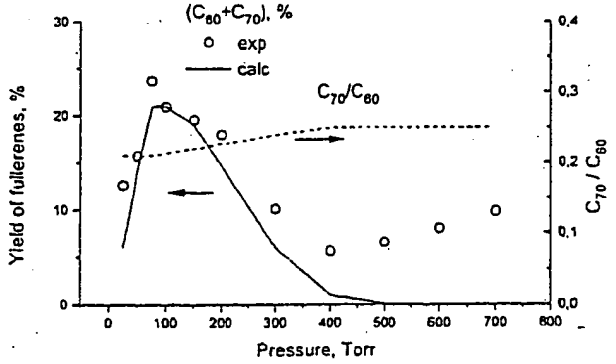


Fig. 5. The helium pressure dependence of the fullerenes yield and the C_{70}/C_{60} molar ratio in the products of the arc synthesis. Comparison of experimental and calculated data. The experimental value for the C_{70}/C_{60} molar ratio is invariably equal to 0.2.

4.1. C1

Noticeable formation of fullerene shells in the turbulent jet begins only after the temperature falls to nearly 2800 K. The main reason is the poor thermodynamic stability of fullerene shells. In such a situation the Stone–Wales reaction could provide an explanation of the high experimental fullerene yields if only the activation energy of this reaction were lower than 70–75 kcal/mol. This limit is much lower than the theoretical estimate of 6–7 eV for the Stone–Wales rearrangement [18]. This fact makes it necessary to account the channels of the growth of the shells directly to perfect fullerene structures passing by the long-lived defect structures in the scheme. It is assumed that proper rearrangement occurs in the very act of this growth reaction.

4.2. C2

Fullerene growth through addition of the C_2-cluster proves to be too slow to provide the experimental yield of fullerenes. The rate constant for this reaction was taken from the equilibrium constant and the measured [17] value of the back reaction. Therefore we include in the kinetic scheme the exchange reaction with participation of the C_3 cluster:

$$C_{58} + C_3 \rightarrow C_{61}^* \xrightarrow{k_{60}} C_{60} + C_1$$

$$C_{61}^* \xrightarrow{k_{60F}} C_{60F} + C_1$$

$k_{60}/k_{60F} = 1.4$ (used in calculations)

A similar path is used for the C_{70F} molecule formation. The highly exothermic addition of the C_3 to the C_{58} yields an energy-rich cluster C_{61}, which readily undergoes monomolecular rearrangements to the most stable structure. At this stage the extra C-atom connected with the proto-fullerene shell can essentially reduce the energy barrier of its reorganisation [5]. In the end of the rearrangement this structure emits the C-atom, thus stabilising the C_{60F} produced against back reactions.

4.3. C3

This scheme of fullerene shell growth has two important distinctions. First, all large even-numbered fullerene shells — say numbered greater than 50 — are included as intermediates in a sole route of sequential growth. Second, the dominating contribution to the overall rate of the clusters growth comes from a single reaction, namely the exchange reaction of the C_3 cluster accomodation to the growing shell. These peculiarities of the kinetic scheme assure the fulfilment of the following equality:

$$\frac{dC_{70F}}{dt} \Big/ \frac{dC_{60F}}{dt} \approx \text{const.}$$

Hereof the constancy of C_{70F}/C_{60F} stems automatically for any conditions of the arc synthesis. The calculations presented in Fig. 5 clearly confirm this thesis.

4.4. C4

Any additional route of fullerene shell growth causes reduction of the fullerene yield value and strong variations in the C_{70F}/C_{60F} ratio upon change of the process parameters.

5. Conclusions

In summary, we draw the following conclusions. The kinetic mechanism of fullerene molecule build-up is likely to be fairly simple. This mechanism can be governed by only a few essential parameters. Two experimental findings discussed in this Letter impose tough restrictions on any hypothetical kinetic scheme proposed. The first is a high yield of fullerenes under optimal conditions and the second is the independence of the C_{70}/C_{60} ratio upon any of the parameters of the arc process.

Acknowledgements

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